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WASTE WOOL AS A SCAVENGER FOR MERCURY POLLUTION IN WATERS

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WASTE WOOL AS A SCAVENGER FOR MERCURY POLLUTION IN WATERS

by

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for the

Office of Research and Monitoring
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Laboratory studies demonstrated the feasibility of using waste wool and wool/polyester blend fibers to remove mercury pollution from waters and bottom deposits. Nylon fiber was shown to have limited potential. Within 24 hours, 90-95% of mercury at the 1-ppm level was removed by the wool fiber. At higher levels of mercury, larger quantities were removed, but the percentage decreased. Changes in pH (2 to 10) and temperature (5 to 35° C) did not markedly alter efficacy of wool, nor did anaerobic conditions or variation in water hardness. However, the presence of sulfide in water or sediment reduced effectiveness of wool. Sources of mercury [redacted] were mercuric chloride, methyl mercuric chloride, phenyl mercuric acetate, bis (2-methoxyethyl) mercury, and dissolved metallic mercury. (Lowry - Texas)

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*Mercury, *Sorption, *Separation Techniques, Sediments, Performance, ~~pH~~, Temperature, Hardness (Water), Anaerobic Conditions, Sulfur, Laboratory Tests, Feasibility Studies, Water Quality Control, Hydrogen ion Concentration

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ABSTRACT

A laboratory study was conducted with a variety of available industrial waste fibers of wool, wool/polyester, and nylon to determine the feasibility of using such fibers to remove mercury from waters and bottom deposits contaminated with mercury. Inorganic and organic sources of mercury were utilized and parameters affecting mercury removal were investigated.

Mercury removed by wool fiber amounted to 90-95% in 24 hours at the 1-ppm level used in the majority of our experiments. At higher levels of mercury, larger quantities were removed up to 300 mg Hg/gram of fiber, but the percentage decreased for a given amount of fiber. Changes in pH (2 to 10) and temperature (5 to 35°C) did not markedly alter efficacy of wool, nor did anaerobic conditions or variation in water hardness. The presence of sulfide in water or sludge reduced effectiveness. Nylon has limited potential as a scavenger for mercury, removing 20-50% of the mercury depending upon circumstances. Waste wool appears to be a potentially useful material for removing mercury from contaminated waters.

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SECTION I

CONCLUSIONS

1. Waste wool fiber was found to be an effective scavenger for mercury in waters over a wide concentration range. More importantly, significant amounts of mercury were taken up by wool from a sample of natural polluted sludge. At the 1-ppm level of mercury in water used in most of our experiments, 90-95% of organic or inorganic mercury was removed within 24 hours. Large quantities of mercury could be removed at higher concentrations up to 300 mg/gram of fiber. Wool fibers function both by themselves and in wool/polyester fiber blends. Accordingly, waste wool has potential for removing mercury from naturally contaminated waters and bottom deposits and provides a use for industrial waste fiber.

2. Nylon fiber is not as effective as wool, removing 20-50% of the mercury depending upon circumstances. No essential difference is noted between the two major types of nylon--nylon 6 and nylon 66.

3. Some variability in the effectiveness of types of wool was found, as would be expected. Wool with certain fiber finishes showed decreased effectiveness but by washing the fiber prior to use, effectiveness could be restored.

4. For practical purposes, wool sorbs mercury species from several sources about equally well. Sources of mercury tested in this program were mercuric chloride, methyl mercuric chloride, phenyl mercuric acetate, bis (2-methoxyethyl) mercury, and dissolved metallic mercury.

5. Variations in pH (2-10) and temperature (5-35°C) do not greatly alter sorption of mercury. Water hardness also has little effect on the effectiveness of wool, and sorption occurs under simulated anaerobic conditions.

6. The presence of sulfide in water or sediment does reduce the efficacy of wool, probably due to the fact that it forms insoluble mercuric sulfide and thereby limits the availability of mercury.

SECTION II

RECOMMENDATIONS

On the basis of the data obtained in our laboratory studies, we recommend two avenues for future work. Possibly both can be carried on concurrently.

The first is to fabricate selected wool fibers into suitable forms (weighted blankets or felts, plugs, nets, etc.) to be placed in field sites with known mercury contamination to measure mercury removal under real conditions. Although several types of wool structures should be tested at first, nonwoven wool felts would be the preferred substrate, since they are inexpensive to make and have good strength and surface area. Appropriate analytical measurements for mercury in the environment and on the fiber would be made, along with determinations of salinity, hardness, temperature, and other properties of the water. Consideration should be given to disposal of the contaminated fibers or chemical reclamation of mercury from them.

The second concerns a more detailed study of factors affecting mercury removal. This might emphasize the role of sulfides and possibly other species not yet investigated. The broader use of wool to scavenge other metallic ions such as cadmium should be included. Methods for increasing the effectiveness of nylon should be investigated, since waste nylon is available in great quantity. Mercury depletion at much lower levels should be investigated.

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SECTION III

INTRODUCTION

Much technical knowledge exists describing the sorption of metallic ions by proteinaceous or keratinaceous materials, chief of which are wool and hair (Appendix A). This attraction between proteinaceous fibers and metals is important to certain technologies such as the old fur and wool felt hat industry, where mercury salts were used to felt wool, and to the textile dyeing and finishing industry, where dyestuffs and finishes containing metallic sites are affixed to fibers.

A paper, "Sorption Behavior of Mercuric and Methylmercuric Salts on Wool," by Friedman, et al., presented at the American Chemical Society Meeting in Los Angeles, March 29-April 2, 1971, describes a laboratory study of various products as sorbents for mercury ions in water. It was concluded that wool was especially effective in removing dissolved mercury under certain conditions and that it might be useful for decontamination.

Therefore, it seems reasonable to utilize keratinaceous or proteinaceous materials like wool as scavengers for mercury salts in water. Besides wool, we include nylon fiber, which can be considered a man-made proteinaceous material. It resembles wool in some respects, due to the presence of amide linkages in the polymer along with amine and carboxylic acid side- or end-groups. Nylon, of course, does not contain the disulfide or sulfhydryl groups found in wool.

The use of such fibers is made more interesting when one considers the large quantities of waste fiber and other proteinaceous materials that are potentially available. Although the use of wool has diminished in recent years, large quantities of waste wool are still available. Growth in the use of synthetic and nonwoven fibers is creating a major solid waste problem. For instance, when synthetic fibers are used in blends with wool, the waste product can no longer be reclaimed. In 1967, about 1.7 billion pounds of textile waste was generated. Wool/polyester blend, a common textile blend, represents a part of this figure. Nylon producers' waste, about 150 million pounds per year, is also reported to be available.

The primary goal of this program was to study the feasibility of using proteinaceous fibers from industrial waste as scavengers for mercury introduced into streams and lakes by contaminated bottom deposits. Although many proteinaceous materials are available, our investigation was limited to wool, nylon, and wool/polyester blend waste.

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To simplify the feasibility study, our work was conducted in the laboratory. We are aware that actual application depends upon certain rate processes in the aquatic environment, degree of contact between protein and mercury, physical form of fiber, etc. Competition for mercury and other sorbable metallic ions between protein fibers and bottom muds certainly would be a final factor in efficacy. However, before these problems can be considered, certain basic information must be obtained in the laboratory. The chemistry of the mercury conversion and use by organisms in the aquatic environment is still a subject of study elsewhere. It has not been our intent to center on the theoretical or the mechanistic nature of the process, but only to demonstrate the efficacy of mercury sorption by the protein materials. We are looking for large effects which would indicate the practical usefulness of the fibers.

Briefly, the program consisted of obtaining representative waste fibers from industrial sources and then measuring the removal of mercury by these fibers from solutions containing a variety of mercury species under a range of conditions that might be expected to influence mercury activity. The parameters evaluated in this study included the following:

Protein Fibers - Wool, nylon, and wool/polyester blend wastes were obtained from commercial textile sources. Because dyeing of fibers can sometimes alter their properties, we inspected both dyed and undyed fibers.

Type of Mercury Compound - For demonstrative purposes, we used mercuric chloride, methyl mercuric chloride, phenyl mercuric acetate, bis (2-methoxyethyl) mercury, and metallic mercury as sources of mercury in solution. Except for the metallic mercury, these compounds are relatively soluble in water. All five might be expected to represent species found in the aquatic environment. Metallic mercury is less soluble than the other compounds but does have some solubility in water. The levels of mercury may, in practice, range from parts per billion (ppb) to hundreds of parts per million (ppm). For most of our work, we selected one part per million as a suitable concentration. The fiber to liquor ratio was selected for the most part to be 1 part fiber to 200 parts of liquid by weight.

pH - We would expect sorption from acid and alkaline waters to be different; therefore, measurements were made in buffered solutions of various pH.

Temperature - Temperature might also be expected to affect sorption. Experiments were made at temperatures of 5°, 23°, and 35°C to observe changes in sorption.

Time - Measurements were made in many cases over a period of hours and days in order to observe sorption behavior of mercury as a function of time.

Quality of Water - Since a variety of other chemical species in water can be expected to affect mercury sorption, we obtained natural waters from known sites in Massachusetts to be spiked with mercury.

SECTION IV

DESCRIPTION OF FIBERS

A selection of typical waste fibers was obtained from industrial sources for use in this work. Their nature and source are identified in Table 1. The three fibers from Arthur D. Little (ADL), Inc., were in-house materials which are not fully identifiable but were employed for introductory work prior to receiving the other industrial fibers. For simplicity, the fiber number and generic descriptions are used throughout the report.

TABLE 1

FIBERS TESTED

Fiber	Description	Source
No. 1	Nylon-66 (100%) fiberstock waste, 1-15 MM, regular, waste reference No. 82840, white	E. I. du Pont de Nemours & Co., Inc. Seaford Plant, Delaware
No. 2	Nylon-6 (100%) reclaimable nylon thread waste, merge 824, white	American Enka Corporation Lowland, Tennessee
No. 3	Nylon-66 soft waste from warper section beam, 40/34/6.0 Z SD T280 Dup. Nyl., Lot No. 1270, white	Vinton Weaving Company Division of Burlington Industries P. O. Box 337 Vinton, Virginia
No. 4	Scoured virgin wool	Buckley & Mann, Inc. Franklin, Massachusetts
No. 5	Virgin polyester staple, 3 denier	Buckley & Mann, Inc. Franklin, Massachusetts
No. 6	Polyester/wool (55%/45%) reprocessed rags, semi-open (picked), in mixed dark colors	Buckley & Mann, Inc. Franklin, Massachusetts
No. 7	Mixed wool knit rags (70-80% wool), semi-open (picked), in mixed dark colors	Buckley & Mann, Inc. Franklin, Massachusetts
No. 8	100% wool comber noils, 70's A/O	Burlington Worsteds Division of Burlington Industries Clarkesville, Virginia
No. 9	100% wool spinning waste (Pneumafil), undyed	Burlington Worsteds Division of Burlington Industries Clarkesville, Virginia
No. 9A	Like Fiber No. 9 but dirtier in appearance	Burlington Worsteds Division of Burlington Industries Clarkesville, Virginia
No. 10	Polyester/wool (60%/40%), waste, code No. ML 105, grade or mix No. 6040 T-65 Dac. 40% wool 64's, color No. tint, name or type is Pneumafil	Burlington Worsteds Division of Burlington Industries Clarkesville, Virginia
No. 11	Virgin wool top, grade 70's	Arthur D. Little, Inc.
No. 12	Polyester/wool blend, dyed	Arthur D. Little, Inc.
No. 13	Virgin nylon stable, type 200	Arthur D. Little, Inc.

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In all, the fibers included virgin wool, used wool, dyed wool, undyed wool, processed wool, polyester/wool blend, polyester, and two types of nylon. Polyester fiber alone was not expected to sorb mercury but was included for comparison with the widely used polyester/wool blends.

The mercury content of selected fibers (Table 2) was measured to assure ourselves that the fibers did not already contain levels of mercury which might influence experimental results. The method of measurement (Procedure 2) and other experimental details are given in Appendix B. The highest level of mercury occurred in wool (Fiber 7) that came from dyed, processed rag materials; by their nature, such materials have a history conducive to sorption of metallic ions from dyebaths, scouring and finishing baths, etc. Polyester/wool (Fiber 6), also from processed, dyed rags, had the next highest level of mercury. Undyed new fibers of polyester/wool (Fiber 10), wool (Fibers 9 and 9A), and nylon (Fiber 1), all exhibited negligible concentrations.

TABLE 2

MERCURY CONTENT OF SELECTED FIBERS

Fiber	Mercury Found μg Hg/g
No. 1 (100% nylon)	<0.04, <0.04
No. 6 (45% wool)	0.36, 0.5[illegible]
No. 7 (80% wool)	1.2, 1.2
No. 9 (100% wool)	<0.04 <0.04
No. 9A (100% wool)	<0.04, <0.04
No. 10 (40% wool)	<0.04 (one sample)

In our work, we ignored the small mercury content of the fibers, since depletion of mercury from a solution containing 1 ppm mercury takes place in any case. In fact, Fiber 7, which contained the highest level of mercury, was found to be among the most active of the scavengers.

SECTION V

SORPTION OF MERCURY BY FIBERS

The various fibers were screened for their effectiveness in reducing mercury levels in solutions prepared with inorganic and organic sources of mercury (mercuric chloride, methyl mercuric chloride, phenyl mercuric acetate, bis (2-methoxyethyl) mercury, and metallic mercury). Substantial amounts of mercury were removed in all cases when wool was present, and greatest removal occurred within 24 hours. The order of effectiveness was wool>polyester/wool>nylon>polyester. Mercury was depleted from both organic and inorganic sources.

The general procedure for determining the propensity of fibers to remove mercury consisted of saturating the fibers in solutions containing appropriate mercury compounds for a given time, removing an aliquot of the liquid, and then measuring mercury content by Flameless Atomic Absorption (FAA) spectrometry--Procedures 1, 4, and 5, Appendix B. All fibers as received were conditioned at 72°F and 50% R.H. prior to use. All our work was carried out in covered polypropylene containers to minimize loss of mercury to the environment (adsorption onto container walls or volatilization into the atmosphere). For each experiment throughout our work, a blank without fiber was run in polypropylene. Loss of mercury to the environment was small but did seem to increase slightly with time. However, since we were concerned with observing large effects with fibers, we used the blanks only for monitoring unexpected deviations which can occur when working with trace amounts of metal ions.

Note that in our work we decided to ascertain sorption of mercury on the fibers by measuring its depletion from solution. We felt that actual analysis of mercury taken up on each fiber represented a time consuming task, since each sample would have to be thoroughly digested to recover mercury. To assess the validity of using mercury depletion from solution as a measure of mercury taken up by the fiber, a material balance between mercury in solution and mercury on the fiber was conducted in selected cases. A conventional bromine oxidation method (Procedure 3) was found suitable for removing mercury from fibers. The recovered mercury could then be analyzed by FAA and balanced against mercury in solution. Data for selected fibers after one week of contact in mercury-containing solutions is shown in Table 3. Within experimental limits, the material balance looks reasonable and indicates that mercury depletion from solution is a valid means of monitoring sorption of mercury by fibers.

TABLE 3

MATERIAL BALANCE

(Results after 1 week contact in µg Hg found, based on whole sample; 200 µg originally in solution)

Mercury Source	Fiber	Measured Mercury Taken up By Fiber	Measured Mercury Removed From Liquid	Percent of Available Mercury Sorbed By Fiber (fiber/liquid)
Mercuric Chloride	No. 4 (100% wool)	160	190	80
	No. 6 (45% wool)	260	190	130
	No. 7 (80% wool)	210	200	100
Methyl Mercuric Acetate	No. 1 (100% nylon)	41,31,20 (30 average)	60	60
	No. 4 (100% wool)	160,239,233 (210 average)	190	110
	No. 6 (45% wool)	180	180	100
	No. 7 (80% wool)	210	190	110
Phenyl Mercuric Acetate	No. 4 (100% wool)	170	190	90
	No. 6 (45% wool)	260	190	140
	No. 7 (80% wool)	188,242,196 (210 average)	190	110

Initially, Fibers 11, 12, and 13 (wool, polyester/wool, and nylon) were used to establish operational techniques (Procedure 4). The results in Table 4 show that the wool rapidly removes mercury from solutions containing a relatively high level of mercury, 50 ppm or 50 µg Hg/ml. In fact, mercury levels at 24 hours had fallen to about the 1 ppm detection limit of the measuring technique using the air/acetylene flame. The remainder of our work was carried out using solutions containing 1 ppm (1 µg Hg/ml), and the more sensitive Flameless Atomic Absorption (FAA) technique was used for measurement.

TABLE 4

DEPLETION OF MERCURY (50 ppm) FROM SOLUTIONS CONTAINING FIBERS

Fiber	Soaking Time (hr)	Measured Concentration of Mercury in Solution (µg Hg/ml)*	
		Mercuric Chloride	Phenyl Mercuric Acetate
No. 11 (wool)	0	51	46
	24	<1	5
	48	<1	4.4
	96	NA	4.4
	168	NA	3.9
No. 12 (polyester/ wool)	0	51	46
	24	12	7.1
	48	5.5	2.7
	96	1.1	2.7
	168	1.1	NA
No. 13 (nylon)	0	51	46
	24	40	32
	48	39	31
	96	37	27
	168	37	23

NA = not analyzed

* Initial concentration = 50 µg Hg/ml

Tables 5, 6, and 7 show the results for Fibers 1 to 10 with three different sources of mercury (Procedure 5). Although all fibers were screened for mercury uptake, they were evaluated in different groups, indicated as experiments A, B, and C. The screening experiments were conducted at ambient laboratory conditions. Experiments A and B were done with unbuffered mercury solutions, while in experiment C the solutions were buffered to pH 6.2, which is close to that found for water saturated with CO_2 from air. Experiments A and B compared fibers in a general way; experiment C provided a more detailed view of mercury depletion with time.

Results from experiment C, which are considered typical, are graphed in Figures 1 and 2. Fiber 7 (wool) removed essentially all of the inorganic mercury almost immediately, and the organic mercury was adsorbed within four hours. Fiber 9 (also wool) removed over 50% of the inorganic mercury within the first several hours and was as effective as Fiber 7 after about 24 hours in removal of organic mercury. Nylon fiber (Fiber 1) was much less efficient in depleting mercury. The controls are the polypropylene containers.

TABLE 5

DEPLETION OF MERCURY (1 ppm) FROM SOLUTION CONTAINING MERCURIC CHLORIDE

Fiber	Experiment	Measured Concentration of Mercury in Solution (μg Hg/ml)*						
		1 hr	2 hr	4 hr	6 hr	24 hr	48 hr	168 hr
No. 1 (100% nylon 66)	A					0.12		0.04
	B				0.64	0.38	0.22	
	C	0.90	0.92	0.92	0.82	0.60	0.64	0.56
No. 2 (100% nylon 6)	A					0.26		0.15
	B							
	C							
No. 3 (100% nylon 66)	A					0.14		0.09
	B							
	C							
No. 4 (100% wool)	A					0.08		0.03
	B							
	C							
No. 5 (100% polyester)	A					0.50		0.64
	B							
	C							
No. 6 (45% wool/50% polyester)	A					0.07		0.04
	B							
	C							
No. 7 (80% wool)	A					0.06		0.02
	B							
	C	0.09	0.07	0.07	0.15	0.05	0.04	0.03
No. 8 (100% wool)	A							
	B				0.52	0.41	0.18	
	C							
No. 9 (100% wool)	A							
	B				0.57	0.59	0.36	
	C	0.47	0.48	0.49	0.46	0.37	0.33	0.21
No. 9A (100% wool)	A							
	B				0.57	0.50	0.30	
	C							
No. 10 (40% wool/60% polyester)	A							
	B				0.37	0.35	0.20	
	C							
Blank (polypropylene beaker)	A					0.47		0.84
	B				1.04	1.04	0.94	
	C	0.97	0.97	0.98	0.96	0.88	0.88	0.74

* Initial concentration = 1.0 μg Hg/ml

TABLE 6

DEPLETION OF MERCURY (1 ppm) FROM SOLUTION CONTAINING METHYL MERCURIC CHLORIDE

Fiber	Experiment	Measured Concentration of Mercury in Solution (µg Hg/ml)*						
		1 hr	2 hr	4 hr	6 hr	24 hr	48 hr	168 hr
No. 1 (100% nylon 66)	A					0.69		0.72
	B				1.00	0.86	0.90	
	C	0.90	0.97	0.94	0.86	0.84	0.82	0.94
No. 2 (100% nylon 6)	A					0.80		0.69
	B							
	C							
No. 3 (100% nylon 66)	A					0.71		0.64
	B							
	C							
No. 4 (100% wool)	A					0.04		0.04
	B							
	C							
No. 5 (100% polyester)	A					0.87		0.88
	B							
	C							
No. 6 (45% wool/55% polyester)	A					0.24		0.09
	B							
	C							
No. 7 (80% wool)	A					0.05		0.04
	B							
	C	0.28	0.18	0.08	0.06	0.07	0.06	0.03
No. 8 (100% wool)	A							
	B				0.09	0.05	0.02	
	C							
No. 9 (100% wool)	A							
	B				0.07	0.03	0.02	
	C	0.75	0.62	0.53	0.38	0.03	0.01	0.02
No. 9A (100% wool)	A							
	B				0.09	0.05	0.02	
	C							
No. 10 (40% wool/60% polyester)	A							
	B				0.16	0.07	0.08	
	C							
Blank (polypropylene beaker)	A					0.83		0.93
	B				1.08	0.93	0.98	
	C	0.96	0.95	0.97	0.94	0.90	0.88	0.98

* Initial concentration = 1.0 µg Hg/ml

TABLE 7

DEPLETION OF MERCURY (1 ppm) FROM SOLUTION CONTAINING PHENYL MERCURIC ACETATE

Fiber	Experiment	Measured Concentration of Mercury in Solution (µg Hg/ml)*			
		6 hr	24 hr	48 hr	168 hr
No. 1 (100% nylon 66)	A		0.66		0.48
	B	0.80,0.84	0.72	0.58	
No. 2 (100% nylon 6)	A		0.50		0.32
	B				
No. 3 (100% nylon 66)	A		0.38		0.20
	B				
No. 4 (100% wool)	A		0.05		0.05
	B				
No. 5 (100% polyester)	A		0.84		0.82
	B				
No. 6 (45% wool/55% polyester)	A		0.18		0.05
	B				
No. 7 (80% wool)	A		0.06		0.03
	B				
No. 8 (100% wool)	A				
	B	0.10	0.05	0.04	
No. 9 (100% wool)	A				
	B	0.06	0.03	0.02	
No. 9A (100% wool)	A				
	B	0.06	0.05	0.03	
No. 10 (40% wool/60% polyester)	A				
	B	0.12	0.06	0.03	
Blank (polypropylene beaker)	A		0.87		0.98
	B	1.10	1.12	0.90	

* Initial concentration = 1.0 µg Hg/ml

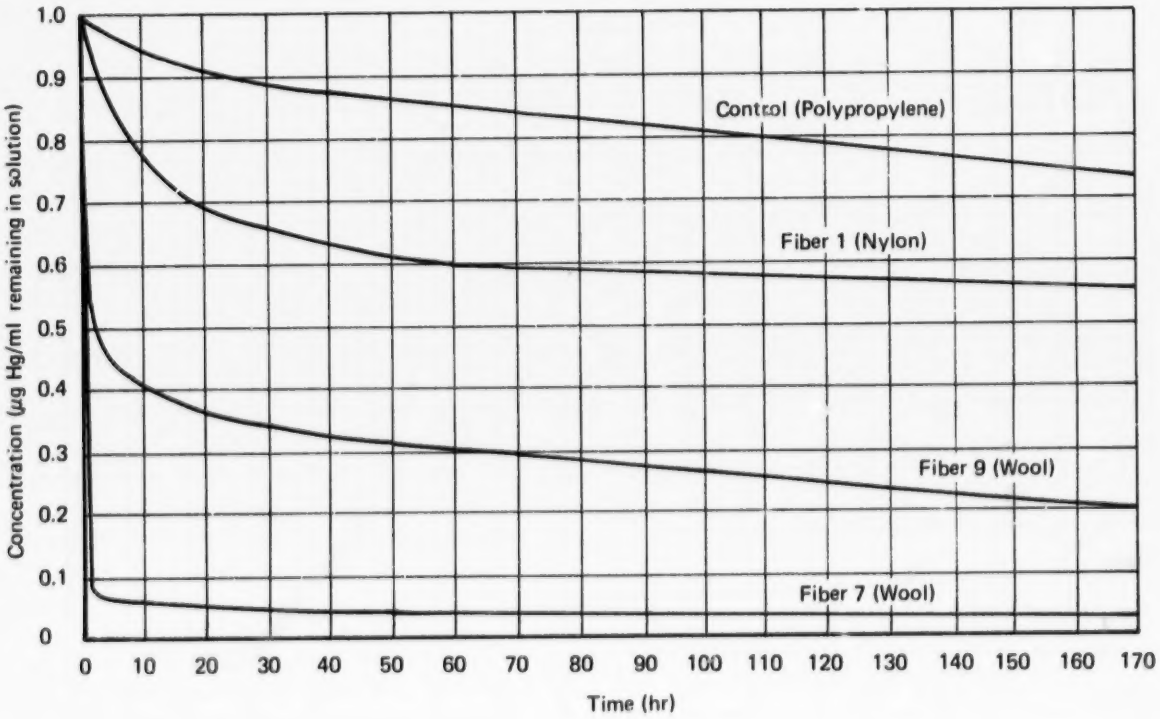

FIGURE 1 DEPLETION OF MERCURY FROM MERCURIC CHLORIDE SOLUTION

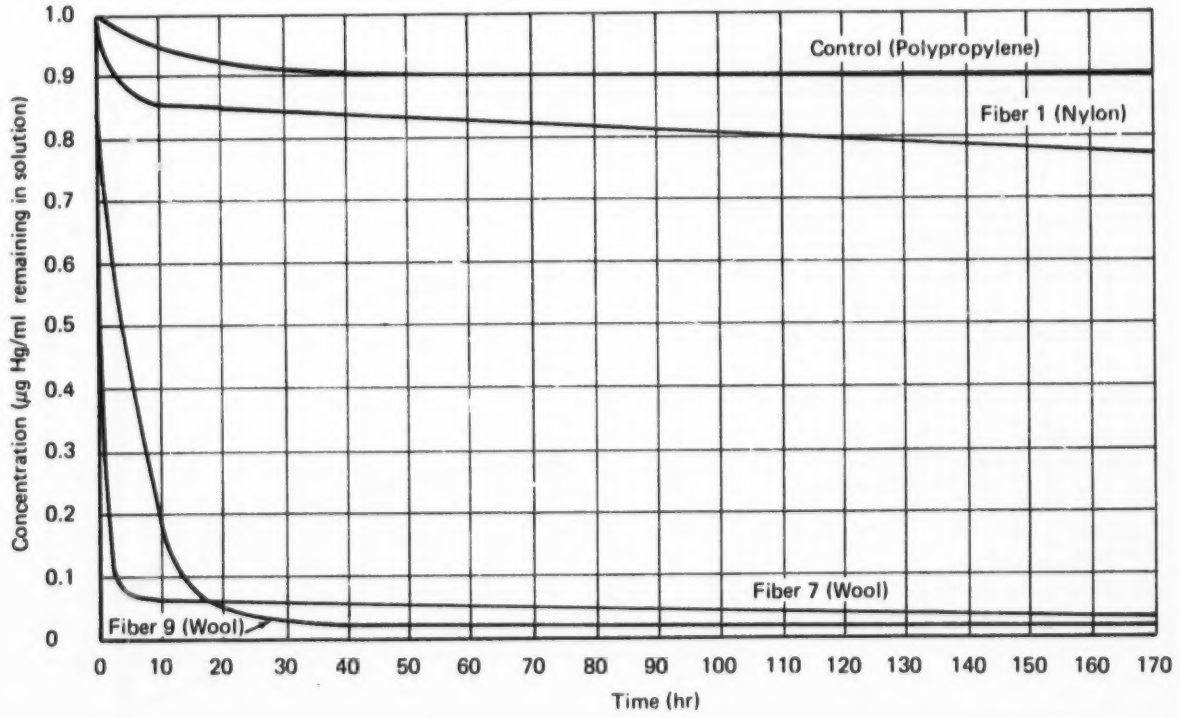

FIGURE 2 DEPLETION OF MERCURY FROM METHYL MECURIC CHLORIDE SOLUTION

With Fibers 1-10, results in the tables generally indicate that wools remove a substantial amount of mercury within 24 hours. The wool in Fibers 9 and 9A, which is characterized by poor sorption compared with other wools, likely contains a fiber finish and was found to be more effective when the finish was removed (Section VI). Nylons appear to be less effective mercury scavengers. Inspection of the data at 168 hours indicates that nylon removes inorganic mercury better than organic mercury. The polyester fiber (Fiber 5) does not remove significant mercury, as indicated when concentration values are compared with appropriate blanks. Note that the low values for polyester and blank in Table 5 appear to be anomalous. Although mercury continues to be depleted from solution after seven days in all cases, the major percentage of depletion occurs during the first 24 hours.

In addition to the three mercury sources already described, fibers were screened in the presence of bis (2-methoxyethyl) mercury and soluble metallic mercury (Procedure 5). The results are listed in Table 8. Again, the wool remains an effective scavenger of mercury, even for solubilized metallic mercury. Note the improvement of Fiber 9 when washed. Like the other salts, the original mercury level was 1 ppm in the case of bis (2-methoxyethyl) mercury. In the case of metallic mercury, the water over a pool of mercury was determined to contain about 60 ppm Hg as solubilized metal, and this solution was adjusted to contain about 1.5 ppm for the other experiment. Assuming in this case that the blank represents 100% of available mercury in solution, we observe Fiber 9 removes 17% of available solubilized metallic mercury and Fiber 7 removes 57%. Thus, Fiber 7 not only has a high capacity for organic and inorganic ionic mercury, but also for solubilized metallic mercury.

TABLE 8

DEPLETION OF MERCURY FROM SOLUTIONS CONTAINING BIS(2-METHOXYETHYL) MERCURY AND DISSOLVED METALLIC MERCURY

(Results are in µg Hg/ml Remaining in Solution After 24 Hours)

Fiber	Bis (2-Methoxyethyl)* Mercury	Metallic** Mercury
No. 7 (80% wool)	0.15	0.65
No. 9 (100% wool)	0.47	1.25
No. 9 (washed - 100% wool)	0.16	
Blank (Polypropylene Beaker)	0.91	1.50

* Initial concentration = 1.0 µg Hg/ml

** Initial concentration = 1.5 µg Hg/ml

SECTION VI

FACTORS RELATING TO MERCURY SORPTION

To gain further insight into the feasibility of using the proteinaceous fibers to scavenge mercury, we investigated in the laboratory various factors which might affect mercury sorption. The results of these investigations are described below.

EFFECT OF pH

To study the effect of pH on the mercury uptake, we decided to use a single buffer which could be adjusted to control pH over a wide range. A multi-component system such as the usual "universal" buffers, which may contain phthalate, chloride, acetate, citrate, carbonate, etc., was not considered desirable due to the many possible interactions and complex formation with the mercury species. In addition, phthalate and acetate are not usually constituents of natural water.

A dilute phosphate solution seemed most appropriate, since it would involve only two of the four possible phosphates (acid, mono, di, and tri salts) at any one pH, it would have some buffer capacity over most of the pH range, and phosphates are natural constituents of water (albeit at low levels).

A concentration of 0.01 M total phosphate was selected, although we recognized that it was higher than normally found in water. We selected pH 4, 6, and 8 as the probable extremes of natural water but also added a few points at pH 2 and 10 to look for any unexpected behavior. The buffered solutions were prepared with the appropriate mercury salts and mercury sorption by fibers was measured in the usual manner (Procedure 6).

Results (Table 9) for the two organo-mercury species are consistent; depletion of mercury from solution appears to be little affected by large variations in acidity. In the case of the inorganic mercury species, depletion seems to be slightly reduced as pH is increased, but effectiveness for removing mercury still remains high. As indicated before, performance of wool Fiber 9 remains diminished unless it is washed.

As a matter of information, the pH of unbuffered mercury solutions used to saturate Fibers 1 to 7 for 168 hours in a previous experiment was measured. In general, for a given fiber, pH remained about the same for solutions of the three mercury compounds (Table 10). In this case, differences in pH among fibers may represent the pH contribution from the fibers themselves.

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TABLE 9

DEPLETION OF MERCURY AT VARIOUS pH
(Measured Concentration of Mercury in Solution, µg Hg/ml at 24 Hours)*

Mercury Source	Fiber	pH					
		2	4	6	8	10	Unbuffered
Mercuric Chloride	No. 1 (100% nylon)	--	0.53	0.60	0.81	--	--
	No. 7 (80% wool)	<0.01	0.05,0.01**	0.07,0.05	0.20,0.15	-- ,0.14	0.08
	No. 9 (100% wool)	0.06,0.02	0.48,0.35	0.45,0.44	0.70,0.57	0.63,0.61	0.57
	No. 10 (40% wool)	--	0.05,0.07	-- ,0.18	0.40,0.40	--	--
	Blank (Polypropylene Beaker)	0.93,0.98	0.93,0.96	0.88,1.01	0.88,1.00	0.98,1.05	0.97
Methyl Mercuric Chloride	No. 7 (100% nylon)	--	0.94	0.94	0.94	--	
	No. 7 (80% wool)	--	0.08	0.06	0.07	--	
	No. 9 (100% wool)	0.04	0.04	0.06	0.04	0.04	
	No. 10 (40% wool)	--	0.10	--	0.09	--	
	Blank (Polypropylene Beaker)	1.04	0.97	1.01	0.96	1.01	
Phenyl Mercuric Acetate	No. 9 (100% wool)	0.03	0.03	0.03	0.02	0.02	
	Blank (Polypropylene Beaker)	0.99	0.99	0.91	0.97	0.97	

* Initial concentration = 1.0 µg Hg/ml

** Replicates

TABLE 10

pH OF UNBUFFERED SOLUTIONS CONTAINING FIBERS
(at 168 Hours)

Fiber	Mercury Compound		
	Mercuric Chloride	Phenyl Mercuric Acetate	Methyl Mercuric Chloride
No. 1 (100% nylon)	6.3	5.0	4.8
No. 2 (100% nylon)	5.9	6.3	5.9
No. 3 (100% nylon)	5.4	5.6	5.3
No. 4 (100% wool)	4.8	4.7	4.8
No. 5 (100% polyester)	4.9	4.5	4.5
No. 6 (45% wool)	5.6	5.5	5.4
No. 7 (80% wool)	4.7	4.6	4.9
Blank (Polypropylene Beaker)	4.9	4.9	4.5

EFFECT OF TEMPERATURE

Fibers 1, 7, and 9 were selected for a study of the effect of temperature on mercury uptake from both mercuric chloride and methyl mercuric chloride solutions. Fibers were saturated at 5°, 23° (room temperature), and 35°C, and data were obtained at 24 and 48 hours in solutions buffered to pH 6.2 (Procedure 7).

The results (Table 11) indicate that mercury depletion increases with increasing temperature within the time period of the experiment. However, a significant temperature effect is not observed for Fiber 7, which is an active scavenger of mercury. Fiber 9, which is shown to have a retarding fiber finish, shows the effect of temperature more markedly. In the case of Fiber 1 (nylon), increasing temperature had a greater effect in depleting the inorganic mercury matter than the organic form. For practical purposes, wool scavenges mercury in both cold and warm water effectively.

TABLE 11

DEPLETION OF MERCURY AT SEVERAL TEMPERATURES
(Results are in µg Hg/ml Remaining in Solution)*

Mercury Source	Fiber	Time (hr)	Temperature 5°C		23°C		35°C	
Mercuric Chloride	No. 1 (100% nylon)	24	0.76		0.70		0.32	
		48	0.60		0.54		0.48	
	No. 7 (80% wool)	24		0.08		0.07		0.07
		48		0.09		0.04		0.04
	No. 9 (100% wool)	24	0.44		0.39		0.12	
		48	0.20		0.12		0.07	
	Blank (Polypropylene Beaker)	24	1.02	1.00	1.14	--	1.00	0.86
		48	0.88	0.90	0.94	--	0.90	0.84
Methyl Mercuric Chloride	No. 1 (100% nylon)	24	1.06		1.06		0.99	
		48	0.67		0.67		0.65	
	No. 7 (80% wool)	24		0.07		0.06		0.05
		48		0.06		0.03		0.07
	No. 9 (100% wool)	24	0.22		0.04		0.07	
		48	0.07		0.02		0.05	
	Blank (Polypropylene Beaker)	24	1.10	0.98	1.14	--	1.00	0.99
		48	0.76	0.98	0.77	--	0.78	0.98

* Initial concentration = 1.0 µg Hg/ml

CAPACITY FOR MERCURY

Two types of experiments were conducted on selected fibers (7, 9, and 10) to examine fiber capacity for mercury. We first measured the total depletion of mercury by fibers as mercury concentration was increased, and then we measured the continued capacity of the fibers to remove mercury repeatedly from a series of 1-ppm solutions.

In the first experiment, one gram of selected fibers was placed in 200 ml of buffered solutions (pH 6.2) containing 5000, 1000, 100 or 10 µg Hg/ml, and mercury depletion from solution was measured in the usual manner at 5, 24, 48 and 96 hours (Procedure 8).

When the concentration of mercury in solution was increased (Table 12), the percent uptake of mercury by a given quantity of wool was reduced, although larger amounts of mercury were sorbed. For a given amount of fiber, effectiveness was greater at lower concentration, but the addition of more fiber might be expected to reduce mercury further. Close inspection of the data indicates in several instances that the amount of mercury in solution increases with time. There is not enough data to determine if this is an anomaly or if sorbed mercury indeed is regenerated from wool. Previous data with 1 µg Hg/ml solutions have always indicated a general loss of mercury with time. As a benchmark, calculations show that one gram of fiber appears to adsorb about 300 mg Hg after 24 hours' soaking in a solution originally containing one gram of mercury. This amounts to about 30% of the mercury. At lower concentrations, about 95% of the mercury is removed from solution.

TABLE 12

DEPLETION OF MERCURY AT VARIOUS CONCENTRATIONS OF MERCURIC CHLORIDE
(Results are in µg/ml remaining in solution;
figures in parenthesis are percent of initial)

Fiber	Initial Concentration (µg/ml)	Concentration at Various Times			
		5 hr	24 hr	48 hr	96 hr
No. 7 (80% wool)	5000	3640(73)	3840(77)	3560(71)	3500(70)
	1000	630(63)	575(58)	545(55)	465(47)
	100	14(14)	4(4)	2(2)	-- --
	10	1.1(11)	0.2(2)	1.5(15)	2.7(27)
No. 9 (100% wool)	5000	3740(75)	3500(70)	3300(66)	3360(68)
	1000	515(52)	455(46)	390(39)	430(43)
	100	5(5)	2(2)	-- --	-- --
	10	0.4(4)	0.4(4)	0.9(9)	2.3(23)
No. 10 (40% wool)	5000	3920(78)	2720(55)	3600(72)	3800(76)
	1000	525(53)	595(60)	580(58)	630(63)
	100	25(25)	5(5)	2(2)	0.5(.5)
	10	0.3(3)	0.6(6)	0.8(8)	0.5(5)
Blank (Polypropylene Beaker)	10	--	--	9.65	9.65

In the second experiment, the fiber samples were saturated five different times, 24 hours apart, in fresh solutions of mercuric chloride containing 1 µg Hg/ml and buffered to pH 6.2 (Procedure 8). Depletion of mercury from solution was measured in the usual manner. When the wool samples were saturated in 1 µg Hg/ml solutions five consecutive times (Table 13), they removed about 95% of the mercury each time. In other words, the wools had taken up about 1 mg of mercury per gram of fiber with no apparent loss of effectiveness for mercury removal at the 1 ppm level.

TABLE 13

DEPLETION OF MERCURY BY FIBERS
WITH REPEATED CONTACT WITH 1 µg/ml MERCURIC CHLORIDE SOLUTION
(Results are in µg/ml Remaining in Solution)

Fiber	Number of Contacts				
	1	2	3	4	5
No. 7 (80% wool)	0.07	0.06	0.08	0.11	0.10
No. 9 (100% wool)	0.37	0.09	0.04	0.04	0.03
No. 10 (40% wool)	0.13	0.05	0.05	0.05	0.05
Blank (Polypropylene Beaker)	0.85	0.88	0.95	0.96	0.93

Although mercury is depleted from solutions with high mercury content, it appears that the efficiency of a fiber increases as the level of mercury decreases.

QUALITY OF WATER

In addition to the other factors investigated, such as temperature and pH, we believed that the quality of water might have an effect upon mercury depletion. For this purpose, we collected four natural waters of varying quality to be artificially contaminated with mercury. All were analyzed for pH and hardness, with the following results:

Source	pH	Hardness (mg/l $CaCO_3$)
Horn Pond, Woburn	7.7	96
Babson Reservoir, Gloucester	6.7	36
From a woodland pond, Sudbury	5.9	10
Atlantic Ocean, off Essex	7.8	1270

The Sudbury water exhibited a yellow color and an obvious sulfidy odor. The other waters had no significant odor or color.

The waters were used as received. They were spiked with mercuric chloride (1 µg Hg/ml) prior to addition of fibers. Measurements at 24 hours were made in the usual manner (Procedure 9).

From the data in Table 14, we can see that water hardness per se and pH had little effect upon mercury depletion, since the wool fibers scavenged to a similar extent in the natural waters and in distilled water, except in the case of the Sudbury water, which was obviously high in sulfur. The sulfide character of this water may have decreased availability of mercury due to formation of a stable complex or it may have decreased the ability of the fibers to adsorb mercury due to interaction with fibers. The decreased blank in this case could indicate formation of insoluble HgS.

TABLE 14

DEPLETION OF MERCURY FROM VARIOUS SPIKED NATURAL WATERS
(Measured Concentration of Mercury in Mercuric Chloride Solution, µg Hg/ml)*

Fiber	Source				
	Woburn	Gloucester	Sudbury	Atlantic Ocean	Distilled** Water
No. 7 (80% wool)	0.08	0.03	0.48	0.06	0.05
No. 9 (100% wool)	0.45	0.45	0.61	0.30	0.37
No. 9 (washed - 100% wool)	0.16	0.05	0.45	0.12	0.10
Blank (Polypropylene Beaker)	0.83	0.95	0.68	0.93	0.90

* Initial concentration = 1.0 µg Hg/ml

** For comparison, data taken from Tables 5 and 16.

ANAEROBIC CONDITION

We ran a brief experiment to see if mercury depletion under simulated anaerobic conditions differed from the depletion commonly observed from solutions saturated with air. Mercuric chloride and methyl mercuric chloride were the choice as model compounds, and Fibers 7, 9, and 9 (washed) were used. Solutions were buffered to pH 6.2 using 0.01 M phosphate. Nitrogen was bubbled through the solutions to displace air and a blanket of nitrogen was maintained over the solutions throughout the experiment. At 24 hours, mercury depletion in solution was measured in the usual manner (Procedure 10).

Depletion data under anaerobic conditions are shown in Table 15 and comparison is made with typical aerobic data. We found no significant difference from data obtained under air-saturated conditions.

TABLE 15

DEPLETION OF MERCURY UNDER SIMULATED ANAEROBIC CONDITIONS
(Measured Concentration of Mercury in Solution, µg Hg/ml at 24 Hours)*

Fiber	Solution			
	Mercuric Chloride		Methyl Mercuric Chloride	
	Anaerobic	Aerobic**	Anaerobic	Aerobic**
No. 7 (80% wool)	0.16	0.05	0.05	0.07
No. 9 (100% wool)	0.45	0.37	0.05	0.03
No. 9 (washed - 100% wool)	0.12	0.10	0.05	--
Blank (Polypropylene Beaker)	1.07	~0.90	1.10	~0.90

* Initial concentration = 1.0 µg Hg/ml

** Aerobic data taken from Tables 5, 6, 16

EFFECT OF WASHING FIBER

Data in previous sections indicated that Fiber 9 (100% wool) did not sorb mercury from mercuric chloride solution as effectively as other wool fibers, although sorption from methyl mercuric chloride seemed normal. This behavior was thought to be due to the presence of a fiber finish which might be hydrophobic in nature. Fiber finishes are normally composed of oils or modified oils and might retard sorption of inorganic materials. To resolve this point, we scoured Fiber 9 and several others with a typical wool cleaning solution composed of detergents to observe how washing of fibers would affect subsequent mercury sorption (Procedure 11). Depletion of mercury from solution was measured in the presence of the washed fibers in the usual manner using mercury solutions containing 1 µg Hg/ml and buffered to pH 6.2.

The data in Table 16 show that washing greatly enhanced the effectiveness of Fiber 9 (as well as that of Fibers 1, 8 and 10); the others were relatively unchanged. Although the wash waters were not chemically analyzed to detect a finish, it seems likely that finishes on these fibers are the cause of the noted behavior.

The Sudbury water exhibited a yellow color and an obvious sulfidy odor. The other waters had no significant odor or color.

The waters were used as received. They were spiked with mercuric chloride (1 µg Hg/ml) prior to addition of fibers. Measurements at 24 hours were made in the usual manner (Procedure 9).

From the data in Table 14, we can see that water hardness per se and pH had little effect upon mercury depletion, since the wool fibers scavenged to a similar extent in the natural waters and in distilled water, except in the case of the Sudbury water, which was obviously high in sulfur. The sulfide character of this water may have decreased availability of mercury due to formation of a stable complex or it may have decreased the ability of the fibers to adsorb mercury due to interaction with fibers. The decreased blank in this case could indicate formation of insoluble HgS.

TABLE 14

DEPLETION OF MERCURY FROM VARIOUS SPIKED NATURAL WATERS
(Measured Concentration of Mercury in Mercuric Chloride Solution, µg Hg/ml)*

Fiber	Source				
	[illegible]	Gloucester	Sudbury	Atlantic Ocean	Distilled** Water
No. 7 (80% wool)	0.08	0.03	0.48	0.06	0.05
No. 9 (100% wool)	0.45	0.45	0.61	0.30	0.37
No. 9 (washed - 100% wool)	0.16	0.05	0.45	0.12	0.10
Blank (Polypropylene Beaker)	0.83	0.95	0.68	0.93	0.90

* Initial concentration = 1.0 µg Hg/ml

** For comparison, data taken from Tables 5 and 16.

ANAEROBIC CONDITION

We ran a brief experiment to see if mercury depletion under simulated anaerobic conditions differed from the depletion commonly observed from solutions saturated with air. Mercuric chloride and methyl mercuric chloride were the choice as model compounds, and Fibers 7, 9, and 9 (washed) were used. Solutions were buffered to pH 6.2 using 0.01 M phosphate. Nitrogen was bubbled through the solutions to displace air and a blanket of nitrogen was maintained over the solutions throughout the experiment. At 24 hours, mercury depletion in solution was measured in the usual manner (Procedure 10).

Depletion data under anaerobic conditions are shown in Table 15 and comparison is made with typical aerobic data. We found no significant difference from data obtained under air-saturated conditions.

TABLE 16

EFFECT OF WASHING FIBERS ON MERCURY SORPTION
(Results Are in µg Hg/ml Remaining in Solution After 24 Hours)*

Fiber	Mercury Source			
	Mercuric Chloride		Methyl Mercuric Chloride	
	Washed	Unwashed**	Washed	Unwashed**
No. 1 (100% nylon)	0.32	0.60	1.0	0.84
No. 4 (100% wool)	0.07	0.08	0.07	0.04
No. 7 (80% dyed wool)	0.03	0.05	0.06	0.07
No. 8 (100% wool)	0.13	0.41	0.06	0.05
No. 9 (100% wool)	0.10	0.37	--	--
No. 10 (40% wool)	0.05	0.37	0.06	0.07
Blank (Polypropylene Beaker)	--	0.88	1.10	0.90

* Initial concentration = 1.0 µg/ml

** Values from Table 4

SECTION VII

MERCURY REMOVAL FROM SEDIMENT

To establish that mercury could be removed by wool from a naturally contaminated sediment, we obtained a sample of bottom sludge taken by JBF Scientific Corporation from a site in the Ashland Reservoir near the Sudbury River. We realize that bottom sludges are biologically and chemically active and that when they are removed from the environment, changes can occur which can affect the mercury species. However, this brief experiment with selected wool fibers (Nos. 7, 9, and 9 washed) indicates the potential usefulness of wool for depleting mercury from bottom deposits even when the mercury is released slowly from the deposit. The rate of removal of mercury from deposits will depend on the solubility of the mercury species.

Mercury measurements were made on solutions in the usual manner and mercury content of sludge and fibers was determined through means of the bromine oxidation step (Procedure 12).

Analyses of the sludge indicated about 48 µg Hg/g and a content of 0.33% sulfur (both on a wet basis). When the sludge was placed in buffered water (pH 6.2) for 48 hours--in one case with stirring and the other case without--and the mercury content of the water was determined, the following values were found:

Stirred	0.02, 0.03, 0.01 µg Hg/ml
Unstirred	0.01, <0.01 µg Hg/ml

Obviously, very little mercury was dissolved.

To determine if wool would remove mercury from this sludge, Fiber 7 was mixed with sludge and water and was allowed to remain eight days. The fiber was removed and washed. Mercury was determined in the fiber and contact solution. The following results were obtained.

Mercury on fibers after immersion	3.20, 3.30, 3.88, 2.84 µg Hg/g (Average = 3.31)
Mercury remaining in solution	0.02, <blank, <blank, 0.01 µg Hg/ml
Mercury content of control fibers	1.18, 0.93, 1.04, 0.82 µg Hg/g (Average = 0.99)

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From the above data, it appears that wool fiber (No. 7) removes 2.3 μg of mercury from the sludge, or 4.8% of the mercury present, in eight days (approximately 0.5% per day). Clearly, transfer of mercury from this sludge to fiber is slow, but nevertheless significant amounts were removed from the sludge and were taken up by the wool.

SECTION VIII

DISCUSSION

MECHANISM OF SORPTION

Two types of mercury takeup can be expected to occur on fibers--that which is truly bonded to the proteinaceous molecule and that which accompanies the takeup of water as the fibers become hydrated. Molecular bonding of mercury is unique for wool and similar fibers and is the basis for the proposed use of wool to scavenge mercury from contaminated waters. Mercury deposited on the fiber from water of hydration is considered a bonus.

The mechanism for sorption of mercury ions by wool and similar materials is a subject for debate. Sorption may be associated with the basic sites, acidic sites, amino sites, sulfur-bearing sites or any combination of these. However, the importance of sulfur in the natural fiber emerges. The high-sulfur fraction of wool, S-carboxymethylkeratin B, is reported to be the matrix or structurally disorganized substance surrounding the microfibrils. It is reported that during treatment of wool with water at 60-100°C, chemical changes occur; cystyl residues (disulfide) are converted to lanthionyl residues (a monosulfide), and the lost sulfur becomes mobile. The sulfur content of wool is 3-4%, and its nitrogen content is 16-17%. Wool was found to scavenge mercury effectively. On the other hand, nylon (a synthetic polyamide having about 16% nitrogen but no sulfur) adsorbs much less mercury, as shown in our work. When sludge or water with a high sulfide content was used, we observed decreased mercury sorption even by wool, indicating that competition exists for the mercury between sulfur in wool and sulfide or other ligands in water.

The contrast in effectiveness between nylon and wool might be further explained by differences in the availability of the fiber molecules to sorb mercury. Wool, a hydroscopic fiber, picks up 10-17% moisture from air at 70°F and 65% R.H. and up to 30% from saturated air. The nylons, on the other hand, pick up only 4-5% moisture at 70°F and 65% R.H. Being less water-sensitive, nylon might be expected to sorb less dissolved mercury because ion mobility is restricted in the essentially hydrophobic nylon fiber. Polyester fiber, which has neither nitrogen nor sulfur and picks up negligible moisture (0.4-0.8% at 70°F and 65% R.H.), removes essentially no mercury from solution.

Although we conclude that for practical purposes wool is an effective agent for depleting mercury from waters, the phenomenon has not been fully explored. The effect of the presence of sulfides in waters should be clarified, as well as the role of fiber hydrophobicity.

FIELD UTILIZATION AND COST

Because our study was conducted in the laboratory, no actual field information is available; nevertheless, we can speculate on means of utilization as well as costs.

Obviously, the fibers require placement into the water close to or on the bottom, since the mechanism for mercury exchange is through solution. Although field use of wool for scavenging mercury might include application in the form of woven cloth structures or bagged fibers, the most practical and economical approach would seem to be through use of nonwoven felt fabrics. Wool felt, one of the oldest forms of fabric, is defined as "a fibrous material built up of interlocked fibers by mechanical and chemical action, moisture, and heat. The blend may consist of wool and other fibers" (The Felt Association, Inc.). Felts can be made in a variety of sizes and with a specific thickness, resiliency, firmness, etc.; they have good strength, water permeability, and fiber surface area; and they are the least expensive cloth structure to produce. If necessary, added strength can be obtained by incorporating nylon fiber or scrim into the wool felt.

The maximum area of felt that can be introduced into the water from a vessel and the best means of conducting the placement will have to be investigated. Conceivably, the felt could be laid from a roll in the boat. The felt would probably require weighting, since the specific gravity of felts is usually less than one. In addition, to insure vertical sinking of the felt, an open pattern or holes may be required in the fabric, which means that a cross-lay of two felts would be required to get full coverage.

After the felts have become saturated an appropriate length of time, they can be withdrawn from the water. The sorbed mercury can then be recovered from the fibers if this seems practical. Bromination or reduction techniques, as well as treatment with citric acid and certain chelating agents, will remove mercury. The efficiency of mercury removal is a subject for future study.

Although it is premature to calculate the cost of laying felt in water and later recovering it, we can estimate the finished cost of felt on the basis of the raw materials and unit production operations. Wool waste is available at 2-12¢/lb, depending upon grade and source; for estimation purposes, we assume that it costs 5¢/lb. The unit operations cost for production of a nonwoven felt is 20-30¢/lb. (We shall assume 25¢/lb.) In the most optimistic case, therefore, we can assume the average raw material and felt costs to total 30¢/lb for a finished felt fabric. For comparison, a woven fabric might cost $1.30 to $1.55/lb to produce.

A 1/4-inch thick felt has a density of 2 to 4 lb/sq yd, depending on firmness. Therefore, to cover one acre (4840 sq yd), we would need 9680 to 19,360 pounds of felt. At 30¢/lb, the estimated cost of 1/4-inch felt to cover one acre would be $2900 to $5800. If a 1/8-inch felt (1 to 2 lb/sq yd) can be used, the cost would be $1500 to $2900; a 1/2-inch felt (3 to 8 lb/sq yd) would cost $4400 to $12,000.

We have found in our work that 1 gram of wool fiber can sorb as much as 300 mg Hg in 24 hours, or 0.3 lb Hg per pound of fiber. If we consider a 1/4-inch felt covering one acre, we have an average quantity of 15,000 pounds of wool present, which means theoretically that 4500 pounds of mercury can be sorbed. Even if the wool is 10% efficient, 450 pounds of mercury could be removed from the environment. Based on the current cost of mercury at $2.40/lb, the potential recovery value, excluding reclamation costs, may be as high as $11,000 per acre, but more importantly, large quantities of mercury can be removed from the aquatic environment.

SECTION IX

ACKNOWLEDGEMENTS

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SECTION X

APPENDICES

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APPENDIX A

LITERATURE SEARCH

At the start of this program, a brief literature search was conducted in recent references and abstracts for new information which might be useful in our work. Sources searched were:

Chemical Abstracts, 1966 to present, a major source;

Applied Science and Technology Index, 1965 to present;

Pollution Abstracts, 1970 to 1971;

Biological Abstracts, 1971;

Nuclear Science Abstracts, 1971; and

Isolated sources such as Chemical Reviews, Chemistry and Industry, Textile Research Journal, and various other periodicals.

The primary reference relating to the use of proteinaceous materials such as wool to recover mercury from waters appears to be that by Friedman, et al. (Source 1 below). The binding of mercury and other heavy-metal salts with various proteins and chemical compounds containing amino groups and sulfhydryl and disulfide moieties is often noted in biochemical papers. Methods of alleviating mercury poisoning in the body often depend on the introduction of such chemicals to combine with mercury. Except to point to the use of proteinaceous fibers for scavenging mercury by analogy, most uncovered references have limited value at this time, and many are purely theoretical studies. Ten are abstracted below to indicate the nature of current literature and are not intended to be inclusive.

1) M. Friedman, C. S. Harrison, W. H. Ward, and H. P. Lundgren, "Sorption Behavior of Mercuric and Methylmercuric Salts on Wool," U. S. Department of Agriculture, Albany, California, 1971. Paper presented before the Division of Water, Air, and Waste Chemistry, A.C.S., Los Angeles, California, March 29-April 2, 1971.

   Describes sorption of mercury by waste wool and other agricultural products to remove mercury from solution. Up to 80% mercury can be removed from solutions of mercuric chloride and methyl mercuric chloride under certain conditions.

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2) "Resin to Purge Mercury from Body," Industrial Research, August, 1971.

Describes use of a synthetic resin containing sulfhydryl groups to remove mercury from mice.

3) Fumiaki Kai, "The Reaction between Mercury (II) and Organic Compounds," Bull Chem Soc Jap, 40, No. 10 (1967), pp. 2297-2302.

Describes reactivities between $HgCl_2$ and basic amino acids and suggests application as means of separating amino acids.

4) S. N. Hemrajani and C. S. Narwani, "Polarographic Study of Metal Ion Complexes with Keratin Fibers (Wool) at pH 4-5 and 30°," J Indian Chem Soc, 44, No. 8 (1967), pp. 704-9.

$HgCl_2$ was thought to combine in molecular form with wool and other salts in ionic form. Chemically modified wool combined with different amounts of a metal. Reduced wool was most effective.

5) A. Weinstock, P. C. King, and R. E. Wutbier, "The Ion-Binding Characteristics of Reconstituted Collagen," Biochem J, 102 (1967), pp. 983-8.

Ion binding qualities of bivalent cations and others from salt solutions were studied, and their relationship to properties of reconstituted collagen was examined.

6) M. Adam, P. Fietzek, Z. Deyl, J. Rosmus, and K. Kuehn, "Investigation on the Reaction of Metals with Collagen in Vivo," Eur J Biochem 3, No. 4 (1968), pp. 415-18.

Mercury reacts in vivo with insoluble collagen to alter its properties.

7) K. C. Tewari, J. Lee, and N. C. Li, "Zinc and Mercury (II) Interaction with Cytidine and Glycylglycine," Trans Faraday Soc, 66 (Pt 8) (1970), pp. 2059-76.

Complexes mercury (II)-cytidine and mercury (II)-glycyl-glycine are formed.

8) M. Matsuda and B. Takeuchi, "The Interaction of Hg++ with Deoxyribonucleic Acid," J Biochem, 61, No. 4 (1967), pp. 523-6.

Describes methods of association of DNA with Hg++.

9) D. F. S. Natusch and L. J. Porter, "Direct Detection of Mercury (II)-Thio-Ether Bonding in Complexes of Methionine + S-Methylcysteine BH Nuclear Magnetic Resonance," J Chem Soc D (10) (1970), pp. 596-7.

Nature of metal-ligand bonds studied showing formation of N Hg+ O and S Hg++ N bonds.

10) D. M. Crothers, "Kinetics of Complex Formation of Nucleic Acids," Stud Biophys 24-25, 79-81 (1970).

Discusses kinetics of Hg (II) binding to nucleic acids.

APPENDIX B

EXPERIMENTAL PROCEDURES

General techniques for conducting the experiments are described in the procedures outlined below. Distilled water was used for preparing solutions, except where otherwise indicated. Mercury salts were standard reagent-grade materials obtained from the following sources:

Mercuric Chloride--obtained from Fisher Scientific Co., Pittsburgh, Pa; certified ACS grade;

Methyl Mercuric Chloride--obtained from Alfa Inorganics, Beverly, Mass., assay 95%;

Phenyl Mercuric Acetate--obtained from Eastman Organic Chemicals Dept., Eastman Kodak Co., Rochester, N.Y.; and

Bis (2-methoxyethyl) Mercury--ADL laboratory compound prepared from reagent-grade mercuric acetate and ethylene gas. Ref: The Chemistry of Organometallic Compounds, by E. G. Rochow, D. T. Hurd, and R. N. Lewis; New York: Wiley (1957), pp. 109 ff.

PROCEDURE 1--FLAMELESS ATOMIC ABSORPTION (FAA) SPECTROMETRY OF SOLUTIONS

The mercury in samples was determined essentially according to the procedure of Hatch and Ott (Anal Chem 40, 2085 [1968]). Two differences are the use of bromine water in place of permanganate solution and the use of hydroxylamine hydrochloride in 1 N H_2SO_4 rather than the use of hydroxylamine sulfate directly. These changes were made due to the nature of the samples and to attain a low background signal.

- Reagents

  a) Stannous sulfate, 10% w/v in 0.5 N H_2SO_4
  b) Sodium chloride, 30% w/v in water
  c) Hydroxylamine hydrochloride, 25% w/v in 1 N H_2SO_4
  d) Sodium chloride-hydroxylamine sulfate solution--add 60 ml of the acidic hydroxylamine solution and 50 ml of 30% sodium chloride solution to a 500-ml volumetric flask and dilute to mark with distilled water.

- Instrumentation-- Perkin-Elmer Atomic Absorption Spectrophotometric Model 303 equipped with a 6" x 1" glass cell with epoxy-sealed quartz windows.

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- Mercury Analysis

a) A known volume of sample was pipetted into a bubbler, which is a 100-ml round-bottom flask containing a 3/4" x 4" well in the bottom into which a tube with a ground glass tip is inserted. (Entire apparatus is called a Smog bubbler, Ace Glass Co.)
b) 1 ml bromine water was added and the solutions were mixed and allowed to stand 5 minutes.
c) 20 ml of NH_2OH-NaCl solution was added and the solutions were mixed and allowed to stand 15 minutes.
d) 10 ml stannous sulfate solution was added, and the bubbler was immediately affixed to the tubing leading to the quartz cell in the AA unit.
e) With the recorder running, the pump to cycle the mercury vapor was turned on.
f) After recorder trace had peaked (usually within 1 to 2 minutes), the inlet line to the bubbler was removed and transferred to the vent line leading to the hood.
g) When the tracing returned to the baseline (indicating removal of all mercury vapor from the cell and connecting tubing), sampling was complete.

To determine the mercury content of fibers, sludge, and other materials containing mercury in unknown states (organic and inorganic), we used oxidation with bromine water prior to FAA analysis as described in the procedures.

PROCEDURE 2--MERCURY CONTENT OF FIBERS

Two 1 g portions of fiber, taken from different places in its bulk, were treated with 50 ml of fresh bromine water for one hour. The solutions were decanted, all the fibers were washed with about 40 ml of water, and the solution and wash were combined and diluted to 100 ml with water. Aliquots (25 ml) were analyzed for mercury via FAA.

PROCEDURE 3--MERCURY BALANCE FROM FIBERS

Fibers were removed from beakers containing the mercury solution and blotted dry between pieces of Whatman #1 filter paper. Weighed portions of the semi-dry fiber were reacted with bromine water in 150-ml beakers for approximately one hour. The solutions were decanted, the fibers were rinsed, and the total solution was made up to a known volume. Aliquots were removed for analysis by FAA.

PROCEDURE 4--INITIAL SCREENING OF FIBERS

Fiber (1.0 g) was saturated in 200 ml of an aqueous solution containing 50 µg Hg/ml of an appropriate mercury compound. The experiments were conducted in covered polypropylene beakers to minimize loss of mercury to its environment. A control without fiber was run in a polypropylene beaker for each experiment. At appropriate time intervals, 10-ml samples of solution were withdrawn and mixed with 1 ml of concentrated HCl. The acidic solutions were stored in capped polyethylene vials prior to mercury analysis by atomic absorption spectrometry using air/acetylene. As the air/acetylene method was replaced in the remainder of the work by the more sensitive flameless method, the former is not described in detail.

PROCEDURE 5--SCREENING OF FIBERS WITH DIFFERENT MERCURY SPECIES

The same method was used as in Procedure 4 with 1.00 ± 0.01 gram samples of fiber, except that the solutions contained 1 µg Hg/ml and Flameless Atomic Absorption spectrometry was used to measure mercury. In experiments A and B, the solutions were not buffered. Experiment C was prepared with a 6.2 pH phosphate buffer. Solutions were prepared with appropriate quantities of mercuric chloride, methyl mercuric chloride, and phenyl mercuric acetate. Solutions containing 1 µg/ml of bis (2-methoxyethyl) mercury were prepared by mixing 10 ml of 20-ppm Hg solution with 190 ml of water buffered at pH 6.2 with 0.01 M phosphate and adding 1.00 ± 0.01 g of fibers for a 24-hour soaking period. Samples were then removed for FAA analysis at the appropriate time intervals.

Some water which had been covering a pool of mercury for several weeks was determined by FAA measurement without addition of a reducing agent to contain approximately 60 ppm Hg as dissolved metal. Five milliliter aliquots of this water were mixed with 195 ml of water buffered at pH 6.2 using 0.01 M phosphate, and 1.00 ± 0.01 g samples of Fibers 7 and 9 were added. The beakers were swirled, and the fibers were allowed to soak in the solution for 24 hours. The samples were removed after 24 hours for analysis by FAA.

PROCEDURE 6--pH EXPERIMENT

Dilute phosphoric acid (0.01 M) was titrated to values of pH close to 2, 4, 6, 8, and 10 using 1 N sodium hydroxide. The resulting solution was diluted tenfold, the actual pH was measured, and 180 ml of the solution was added to polypropylene beakers containing 1.00 ± 0.01 g of the selected fibers. Mercury salt solution (20 ml of 10-ppm solution) was added by pipet, and the beaker was swirled to obtain mixing of solutions. Samples of solution (10 ml) were removed after 24 hours of contact with fiber, and the mercury remaining in solution was determined

by FAA. Beakers containing only solutions of salts at the various pH's served as controls. A pH meter was used to make the measurements.

PROCEDURE 7--TEMPERATURE EFFECT

Two hundred milliliters of buffered (pH 6.2, 0.01 M phosphate) solution containing 1.0 µg Hg/ml was mixed with 1.00 ± 0.01 g of fiber in a 400-ml polypropylene beaker. Beakers were kept at 5°C, room temperature (approximately 23°C), and 35°C prior to adding fiber. Samples were removed after 24 and 48 hours at the three temperatures, and the remaining solutions were analyzed for mercury by FAA.

PROCEDURE 8--MERCURY CAPACITIES

• Total Capacity--Each fiber sample (1.00 ± 0.01 g) was placed in a 400 ml polypropylene beaker, and 200 ml of solution containing either 5000, 1000, 100, or 10 µg Hg per ml of buffered solution was added. The beakers were swirled, covered with watchglasses, and allowed to stand. The 5000 and 1000 µg/ml Hg solutions were prepared using weighed amounts of mercuric chloride dissolved in pH 6.2, 0.01 M phosphate buffer. The 100- and 10-µg concentrations were prepared by appropriate dilutions of the concentrates. Samples were taken after 5, 24, 48, and 96 hours' soaking time. The beakers were swirled to ensure solution homogeneity just before sampling, and 0.1 ml of concentrated HCl was added to each sample removed to prevent loss of mercury to the container. Mercury measurement was by FAA.

• Repeat Contact Capacity--A 200-ml quantity of solution containing 1 µg/ml of mercuric chloride was buffered to pH 6.2 with 0.01 M phosphate. Fiber (1.00 ± 0.01 g) was soaked in this solution for 24 hours. The beaker was swirled, and a sample was removed for analysis. The remainder of the solution was decanted, the fiber was squeezed to remove excess liquid, and a fresh 200 ml of 1 µg Hg/ml, pH 6.2, solution was added to the now one-day old fiber. This process was repeated for each fiber over a five-day period. The mercury content of the samples was determined by FAA.

PROCEDURE 9--WATER QUALITY

Each water sample (180 ml) was mixed with 20 ml of a solution containing 10 µg Hg/ml (as $HgCl_2$) to give a concentration of 1 µg Hg/ml. Fiber (1.00 ± 0.01 g) was added, and the beakers were swirled and allowed to stand 24 hours. The beakers were again swirled just before the solutions were subjected to FAA analysis for mercury.

PROCEDURE 10--ANAEROBIC CONDITION BUFFERED TO pH 6.2

Nitrogen was bubbled through 200 ml of solution containing 1 µg Hg/ml to displace oxygen. Fiber (1.00 ± .01 g) was added and purging was continued for 3 to 4 minutes. During the 24-hour saturation period, a blanket of nitrogen was maintained over the beakers in a glove bag filled with nitrogen. Aliquots of liquid were then removed, and the mercury was measured by FAA.

PROCEDURE 11--FIBER WASH

Wash solution--Trisodium phosphate		0.3 gram
	Triton X-100	0.1 gram
	Tap water (110°F)	1000 ml

Fibers (15 g) were placed in the hot solution and periodically stirred over a 30-minute period. They were then removed, squeezed, thoroughly rinsed in warm tap water, and dried at 72°F, 50% R.H. The fibers were tested in the usual way in solutions containing 1 µg/ml of mercury as mercuric chloride and methyl mercuric chloride. Both solutions were buffered with 0.01 M phosphate to pH 6.2. Fiber (1.00 ± 0.01 g) was soaked in 200 ml of the above solutions for 24 hours. Samples of the liquid were then removed for mercury analysis by FAA.

PROCEDURE 12--SEDIMENT EXPERIMENTS

Two 1.0 g samples (wet basis) of sludge were reacted with 50 ml of bromine water for 1 hour to oxidize all available mercury. The sludge was then filtered and washed. Final filtrate and wash volume was 100 ml. Aliquots were removed and mercury determined by FAA. Four 1.0 g samples (wet basis) of sludge were added to four beakers, each containing 200 ml of water at pH 6.2 (0.01 M phosphate buffer). Two of the mixtures were stirred, the other two were unstirred. Samples of water were removed after 48 hours and analyzed for mercury in the usual way.

In another experiment, four samples of fiber (1.0 ± 0.01 g) were placed in the mixture of sludge (1.0 g) and water (200 ml), buffered to pH 6.2 with 0.01 M phosphate, and allowed to remain for eight days. The fibers were rinsed with water to remove particulate and then reacted with 50 ml of fresh bromine water for 5 hours. The solution was decanted into a 100-ml volumetric flask, the fiber was washed four times, and the rinses were combined with the decanted liquid. Mercury was determined by FAA. As controls, four fresh samples of fiber (1.00 ± 0.01 g) were reacted with bromine water and their mercury content was determined. The solution in contact with fiber and sludge was also analyzed for mercury.

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Laboratory studies demonstrated the feasibility of using waste wool and wool/polyester blend fibers to remove mercury pollution from waters and bottom deposits. Nylon fiber was shown to have limited potential. Within 24 hours, 90-95% of mercury at the 1-ppm level was removed by the wool fiber. At higher levels of mercury, larger quantities were removed, but the percentage decreased. Changes in pH (2 to 10) and temperature (5 to 35°C) did not markedly alter efficacy of wool, nor did anaerobic conditions or variation in water hardness. However, the presence of sulfide in water or sediment reduced effectiveness of wool. Sources of mercury used were mercuric chloride, methyl mercuric chloride, phenyl mercuric acetate, bis (2-methoxyethyl) mercury, and dissolved metallic mercury.

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